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PROBATION AND PRESERVATION
OF TIMBER AND STREAMS



ARMAND J. VAN DER MYN



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CORROSION AND PRESERVATION
OF IRON AND STEEL

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FIRST EDITION

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By

ARMAND J. P. VANDERMYN

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DEDICATION

TO THOSE WHO HAVE IN THE PAST,
AND TO ALL THOSE WHO
WILL IN THE FUTURE, CONTRIBUTE TO PROGRESS
IN GENERAL AND THE PRESERVATION OF
IRON AND STEEL IN PARTICULAR,
THIS BOOK IS RESPECTFULLY
DEDICATED



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INTRODUCTION



THE protection against corrosion of iron and steel is a problem to which has been given more thought and study in the past five years than in the previous five hundred years. Many eminent authorities have conducted their investigations both from a practical and theoretical point of view, and the conclusions arrived upon have the support of many practical men.

The writer has conducted a number of experiments and while in some instances it was difficult to absolutely determine the influence which electricity brings to bear upon the corrosion problem, enough evidence has been secured to accept the electrolytic theory of corrosion as the correct one. It is the aim of the writer to discuss in this booklet the electrolytic theory of corrosion and present for your consideration an outline of the cause and prevention of the most insidious enemy of iron—Rust.

PITTSBURGH
OCTOBER 1st, 1921



CORROSION AND PRESERVATION OF IRON AND STEEL



CHAPTER I

Why Iron and Steel Should be Protected



It is not within the power of any man to predict the future, and to say in these days of progress, substitution and discovery that our supply of iron ore will become exhausted, is perhaps saying too much. Nothing, however, can be gained by ignoring facts.

When we consider that the annual production of pig iron in the United States alone grew from about 14,000,000 tons in 1900 to about 55,000,000 tons in 1920, one may well ask, "How long will the world's ore supply stand the drain upon it?" Enormous quantities of the finished product are allowed to

perish yearly for lack of adequate protection, and unless civilization learns to protect and preserve its stores of iron and steel already manufactured, future generations may be compelled to find either a substitute for iron or develop a process by which non-corrodible iron can be manufactured. It is gratifying to observe that this important problem is receiving the thoughtful attention of many learned bodies, metallurgists and engineers, and while progress has been made in regard to manufacturing iron and steel resistant to corrosion, the problem has by no means been solved, and until it has we must depend upon protective coatings.

During the past twenty years the demand for steel has increased enormously not only in America but in the world. Last year's exports of iron and steel products had a total value of \$1,100,000,000, and in the same year more than 20,000,000 tons of pig iron were produced in the furnaces of England, France, Germany and Belgium.

What the next twenty years will bring is of course a matter of conjecture, but it seems fair to

assume that the demand for steel will increase tremendously.

Millions of tons of reinforcing steel will be used in the construction of the Nation's highways, to say nothing of the immense tonnage of structural steel which will be fabricated into bridges crossing the rivers and valleys over which these highways will run.

Other millions of tons of structural steel will be required for the erection of modern fireproof skyscrapers to house our ever-increasing population, to provide office buildings where the world's business can be transacted, to build hotels, railroad terminals, factories, bridges, subways, ships—in fact, a thousand and one things necessary for modern civilization, and steel is the one product which can meet the demand.

Can anyone imagine the plight of civilization if it were denied the utilization of steel?

Can anyone advance reasons why we should not protect against corrosion every square foot of steel or iron produced?

Is there any reason why those who are devoting their time to the designing and creating of new steel structures should not take all precaution to see that the steel is properly protected against corrosion, and thus preserved?

Is there any reason why those charged with the maintenance of steel structures should not be thoroughly conversant with the best possible means of protection? We think not.

“A penny saved is a penny earned” is a saying with which all of us are acquainted, but not all of us realize that to preserve a ton of steel from destruction means not only a saving of the iron ore, but also the conservation of about four tons of coal.

This point was forcibly brought out in Edwin E. Slosson's book, “Creative Chemistry”, wherein he says, “Every year the blast furnaces of the world release 72,000,000 tons of iron from its oxides and every year a large part, said to be a quarter of that amount, reverts to its primeval forms. If so, then man after five thousand years of metallurgical

industry has barely got three years ahead of nature, and should he cease his efforts for a generation there would be little left to show that man had ever learned to extract iron from its ores. The old question, 'What becomes of all the pins?' may be as well asked of rails, pipes and threshing machines. The end of all iron is the same. However many may be its metamorphoses while in the service of man, it relapses at last into its original state of oxidation. To save a pound of iron from corrosion is then as much benefit to the world as to produce another pound from the ore. In fact, it is of much greater benefit, for it takes four pounds of coal to produce one pound of steel, so when a piece of iron is allowed to oxidize it means that four times as much coal must be oxidized in order to replace it. And the beds of coal will be exhausted before the beds of iron ore.

If we are ever to get ahead, if we are to gain any respite from this enormous waste of labor and natural resources, we must find ways of preventing the iron which we have obtained and fashioned into useful tools from being lost through oxidation."

The aim of man is to create, to beautify and make permanent the fruits of his labor; then why should we spend large sums of money and years of work designing and erecting a steel structure,—be it a skyscraper, a manufacturing building, or a bridge,—only to allow the steel to revert back to that from which it was won—rust?

Iron is the most useful of all metals. Its employment in our everyday life is as necessary as is the food we eat. Without iron and coal, civilization would be in a sad plight, and it is reasonable to believe that man will realize the necessity of protecting against destruction the world's most valuable product.

CHAPTER II

The Electrolytic Theory of Corrosion

Many experiments, actual observation and careful study seem to have established with reasonable certainty that corrosion of iron and steel is due to an electro-chemical action, and to those of us who have studied the subject, the explanation is not a very difficult one to understand.

In order to thoroughly appreciate the importance of the electrolytic theory it is essential to bear in mind that iron has a certain solution tension, even though the iron is chemically pure and the solvent is pure water. This solution tension may be modified by impurities present in the iron or the solvent, and again may be exhaltated by certain substances that come in contact with the iron.

Whitney (I) described the subject in a very interesting manner, embodying in his argument the interpretation of Nernst concerning the source of electro-motive force between a metal and a

(I) Loc.cit., p. 38.

solution. "When a strip of metallic iron is placed in a solution of copper sulphate, iron passes into solution and copper is deposited, this change being of course accompanied by a transfer of electrical charge from the ions of copper to those of iron. Hydrogen acts as a metal and is electrolytically classed with copper in relation to iron. If, therefore, we immerse a strip of iron in a solution containing hydrogen ions, an exactly similar reaction will take place, iron will go into solution, and hydrogen will pass from the electrically charged or ionic to the atomic or gaseous condition. In such a system the solution of the iron, and, therefore, its subsequent oxidation, must be accompanied by a 'precipitation' or setting free of hydrogen. It is very well known that solutions of ferrous salts as well as freshly precipitated ferrous hydroxide are rapidly oxidized by the free oxygen of the air to the ferric conditions, so that if the electrolytic theory can account for the original solution of the iron the explanation of rusting becomes an exceedingly simple one."

The application of the electrolytic theory in connection with the theory of solution will be better understood when we consider that slight segregation in the metal, or even unequal stresses and strains in the surface will throw the surface out of equilibrium, with the result that the solution tension will be greater at some points than at others. In other words, a point of maximum and a point of minimum solution pressure will be established. The point of maximum solution pressure will be electro-positive to the point of minimum solution pressure and a current will flow from one point to the other, provided the points are in electrical contact by means of a conducting film. This conducting film may be water, in which case corrosion will be very much excited, or conductivity may be provided by means of a substance contained in the protective coating, or, again, through the inability of the protective coating to prevent moisture from penetrating through the coating and thus allowing moisture to come in direct contact with the steel or iron. In the event that a so-called protective

coating is not entirely free from pores, or contains substances capable of conducting electric current, it will stimulate rather than prevent corrosion simply because the moisture it allows to penetrate will cause the iron over which it is applied to pass into solution in the electro-positive areas.

Much light was thrown upon this important subject by Walker (I), who states as follows. "When a piece of iron is placed in ordinary water, exposed to the air, it will dissolve or rust. If now there be placed in the water with this piece of iron a piece of platinum, the solvent or corroding action of the water will not be changed. The oxygen is present in the solution as before, and the iron ions as they separate from the metallic iron are being oxidized and precipitated as rust. If now the platinum and iron be electrically connected, a marked increase in the rate of the solution or corrosion of the iron is noticed. No chemical condition has been changed; the difference lies in the fact that there is now an electrical contact between the iron and

(I) Jour. Iron and Steel inst. 1909.

the platinum, and the platinum furnishes a surface on which the hydrogen can deposit, and on which, by virtue of its catalysing action, the hydrogen will be rapidly oxidized by the dissolved oxygen, and thus removed from the sphere of action."

It was believed that owing to the fact that the mass metal and solution are of opposite polarity the electrolytic tension became so great that no more atoms could escape to the ionic state and that therefore the solvent action would cease, but Helmholtz described a theory called by him the electrolytic double layer which provided information of great value. If according to this theory (I), there be in the water ions of another metal which has a smaller solution pressure than the one under consideration, the ion with the less solution pressure will pass back to the metallic state, plating out on the first metal and giving up its charge of electricity. At this point the first metal will be charged positively, and the solution in the immediate vicinity negative, and there will tend to be

(I) Corrosion and Preservation of Iron and Steel, Cushman & Gardner, p. 27.

set up a second electrolytic double layer opposite in polarity to the first. The result is, a current of electricity flows from the metal to the solution at the point where the metal passes into solution, through the solution to the metal at the point where the ions of the second metal are plating out, and back through the first metal to the starting-point again. The electrolytic double layers are thus destroyed, an electric current passes, and the solvent action of the water on the first metal continues.

Careful observation tends to support this theory. The corrosive action of iron and steel is not arrested until the fundamental cause of it is removed, and so far as the writer is able to state the influence of both water and oxygen upon steel and iron is detrimental to its preservation.

There may be some difference of opinion as to the continuation of the solvent action, but that iron and steel cannot rust in water unless oxygen is present or in oxygen unless water is present is pretty well recognized as an established fact.

It is of course well to recognize that the solvent action of water may be either modified or stimulated depending upon impurities present in the solvent. Thus, for instance, waters containing carbonic and sulphuric acids will stimulate the action of corrosion to a remarkable degree, while any railroad bridge engineer will be able to testify that the sulphurous gases, liberated through the combustion of coal, play havoc with his steel bridges. Rain water seems to have a peculiarly destructive action upon steel, which is probably due to the carbonic acid present, and mine waters, containing as a rule, large quantities of sulphur, are very violent in their action upon steel.

Those who have observed the condition of steel or iron exposed to sea water or the so-called salt water spray, will admit that corrosion of such steel is violent and rapid and steelwork thus exposed requires positive protection if it is to survive.

Sea water contains soluble salts which are readily and easily ionized, which no doubt accounts for the energetic galvanic action and the subsequent pitting

and rusting of the steel with which it comes in contact. The protection against corrosion of steel exposed to sea water is a subject which is receiving careful consideration, and will be discussed specifically in another chapter. It is worthy of mention here, however, that the electrolytic theory of corrosion is closely related to this particular problem.

While escaped currents from high potential power and light circuits undoubtedly aid in, or aggravate, the corrosion of iron, the popular belief that outside electrical forces are necessary to produce electrolytic action, is not in accordance with facts.

In "Corrosion and Preservation of Iron and Steel" by Cushman and Gardner, the following explanation concerning electrolysis is presented:—"The phenomenon known as electrolysis takes place whenever a current of electricity passes through a solution capable of conducting the current. Such a solution is known as a conductor of the second class to distinguish it from an ordinary conductor like a metallic wire, which is of the first class. A solution of sugar will not conduct a

current of electricity while a solution of salt will readily do so. This difference in behavior is accounted for by the fact that the salt is dissociated into ions while the sugar is not. A substance which in solution will conduct electricity is known as an electrolyte. The phenomenon of electrolysis shows that when a current is passed through a solution of an electrolyte, there is a mechanical movement of the ions towards the electrodes. Thus, if a current is passed through a solution of hydrochloric acid the positive hydrogen ions will proceed to the negative electrode where they will plate out after giving up their electrical charges. Having now assumed the atomic or gaseous condition, the hydrogen escapes from the system in the form of minute bubbles. While this action is occurring at the negative pole an equivalent amount of chlorine is being plated out and disengaged at the positive pole.

It is not necessary that an outside or external source of electricity should be at work before electrolysis can take place. If two strips of dissimilar

metal are plunged part way into a solution and connected by a wire, or by any other means, across the top, a current will flow around the circuit. This current is generated at the expense of the more electro-positive metal in the couple. The electro-positive element rapidly shoots off positive ions into the solution, thereby leaving itself negatively charged so that it invariably appears as the negative pole in the circuit. Even two steel needles from the same package are sufficiently dissimilar to show a slight difference of potential when coupled in such a way, and one will be protected while the other suffers accelerated corrosion. From the standpoint of the electrolytic theory all iron and steel must be thought of as a composite structure, as though, indeed, it was compounded of more or less well-consolidated bundles of more or less homogeneous needles or units."

There seems to be some difference of opinion among authorities on the subject of corrosion—whether electrolysis is alone responsible for the rapid corrosion of modern steel, or whether present

methods of manufacturing steel is contributing its share to the ever-increasing corrosion problem. H. M. Howe, pleading for modern steel, (I) states as follows:—"The fact that steel has come into wide use simultaneously with a great increase in the sulphurous acid in our city air and of strong electric currents in our city ground may well lead the practical man, be he hasty or cautious, into inferring that the rapid corrosion of today is certainly due to the new material of today, steel, whereas, in fact, it may be wholly due to the new conditions of today, sulphurous acid and electrolysis."

In discussing corrosion of modern steel, Sang, (II), says:—"Carelessness of manufacture, which tends to heterogeneousness, is an invitation to corrosion, and in itself goes far to explain why modern steel, which is tortured into shape at such a high speed that the molecules are not permitted to readjust themselves, is said to be more corrodile than the metals produced a generation ago; in

(I) Proc. American Society for Testing Materials, 1906, VII, 155.

(II) Proc. Eng. Soc. West. Pa., XXIV, 10, p. 511.

those days iron and steel were produced in small quantities, without the addition of other metals, and were rolled slowly and allowed to cool naturally. The internal strains due to mechanical treatment are not to be confounded with the unevennesses in the distribution of the impurities due to segregation in cooling; these mechanically induced strains are really equivalent to straining the metal beyond the elastic limit, which makes it more corrodible. Moreover, the tonnage-craze, from which the quality of product in so many industries is today suffering, is causing to be placed on the market a great mass of material, only a small proportion of which is properly inspected, which is not in proper condition to do its work—rails and axles which fail in service and steel skeletons for high buildings which may carry in them the germs of destruction and death.”

While it cannot be denied that the hand-wrought iron of the past was more resistant to corrosion than is our modern steel, yet the present demand for, and various uses of, steel prohibits the return to the old

process of hand-wrought iron, and our problem to-day is to find means to manufacture steel highly resistant to corrosion, without reverting back to the tedious process of earlier days.

Civilization cannot go back—it must find modern methods for modern problems; it must meet conditions as they arise, and while striving to produce purer, less corrosive steel, it must preserve against destruction the countless steel structures now in use and those to be erected.

CHAPTER III

Prevention of Corrosion

When considering the prevention of corrosion of iron and steel by means of a protective coating, it is essential to bear in mind the now universally accepted fact—namely, that corrosion is due to an electro-chemical action.

Furthermore, we must not lose sight of the certainty that iron and steel cannot rust unless it comes in contact with both water and oxygen.

It goes without saying, then, that the first requirement of a protective coating should be its ability to prevent both moisture and oxygen from reaching the surface of the steel or iron.

The second requirement is that neither the pigments nor the vehicle contain materials which are conductors of electric current, or oxygen-carrying agents.

In a paper, (I), “Conditions that Must Be Met in the Ideal Paint for Railway Bridges”, Mr.

(I) Proc. Third Annual Convention Maintenance of Way Master Painters' Assn. of U. S. & Canada, Nov., 1906.

Edward Hurst Brown had the following to say: "The most insidious enemy of the iron bridge is rust, and the primary object of painting is to protect it from those elements which cause destruction by rust. Rust is caused by the combination of the metal with oxygen to form hydrate oxide of iron. This oxygen may be obtained from the air, from water, or from some other substance which acts as a carrier of oxygen or an oxydizing agent—always however, in the presence of moisture. Now, one of the primary things to be considered in choosing a paint for ironwork is that it shall not contain in its pigment or vehicle any substance which is chemically active in such way as to convey oxygen to the iron. For if such a chemically active agent be introduced into the paint, sooner or later it will promote rather than prevent rust. Of course, so long as the oil, in an oil paint, remains intact, it envelops the particles of pigment and keeps them away from the iron, but in time the oil, which has hardened by absorbing oxygen from the air, begins to disintegrate by the action of water coming from

rain, hail, snow, or fog. Moreover, even the freshly applied oil is not absolutely impenetrable to moisture, as has been shown by numerous experiments, and, however completely the particles of the chemically active pigment may be covered by an oil film, they will necessarily come in contact with moisture—will decompose the water and absorb its oxygen, and convey it, together with the hydrogen, to the surface of the iron to cause rust. For this reason, the ideal paint for a steel or iron bridge should not contain a chemically active pigment, nor any strongly oxidizing agent in the way of driers.”

It will be noted that Mr. Brown makes no mention of the electrolytic theory, but it is plain from this article that even before the electrolytic theory became understood, authorities realized that pigments incorporated in oil were instrumental in the stimulation of corrosion.

Pigments can stimulate corrosion in three different ways, and for convenience sake, it may be well to classify the different actions:

CLASS 1.—In this class are included pigments which, by virtue of their catalytic action upon the

oil, cause extreme oxidation of the oil film in which they are incorporated. This action, of course, shortens the life of the oil, and permits moisture to come in contact with the pigments. By decomposing the water and absorbing its oxygen, these pigments then become active in stimulating corrosion by conveying to the iron or steel both hydrogen and oxygen.

CLASS 2.—In this class we have pigments which are known to be conductors of electric current. The use of such pigments will provide a conducting film between the point of maximum and minimum solution pressure, with only one result—the formation of auto-electrolysis, commonly known as rust. There are also included, pigments (various forms of carbon) which, because they so retard the drying of linseed oil, demand an excessive amount of dryer to be added to the oil, thereby causing the oil to oxidize too rapidly, and necessarily shorten its usefulness as a water-excluder.

CLASS 3.—This class represents pigments which are chemically inactive, have no harmful effect

upon linseed oil, and really are inhibitive in character, but they have one weakness—they are soluble in water, which makes them undesirable for use in structural iron paints.

It must be remembered, however, that while pigments in a paint have a definite mission to perform, their proper selection is of no greater importance than is the extreme caution which the production of the vehicle demands.

The writer has stated that the life of a paint is dependent upon the life of the oil in which the pigments are ground, and he is not yet ready to retract that statement.

The paint manufacturer who wants to produce an honest anti-rust paint must direct all his research to perfecting a combination of pigments which will not interfere with the natural life of the vehicle, and he must further produce a vehicle having maximum durability.

It is well known that linseed oil, when used alone, is not entirely free from pores, and while no other oil which can entirely replace linseed oil is available,

yet a combination of linseed oil and china wood oil, properly proportioned, reinforced with selected varnish gums, fused together under expert heat treatment, produces a vehicle which is much superior for use on steel and iron than is a straight linseed oil.

China wood oil is extracted from the nuts and seeds of the Chinese tung tree, and when properly treated at certain temperatures, produces an oil which is well-nigh water-proof. The finished product dries with a hard, durable film, and those who understand its manipulations consider its use in high-grade structural iron paint of incalculable value.

It is certain that in the making of marine and water-proof paints, china wood oil is indispensable.

The average man, not familiar with the paint and varnish industry, is apt to consider the presence in paint of any but linseed oil an adulteration, mainly because he considers that the use of such oil is resorted to on account of a cost consideration. Whatever may be the facts regarding

the use of some oils, the use of china wood oil never cheapens the manufacturing cost of a paint, because even in its raw state, china wood oil is seldom cheaper, and more often, its cost exceeds that of linseed oil. When to this, the cost of treatment and manipulation is added, it will be seen that its use is not suggested because of lower cost, but solely because of the added life it gives to the paint.

To china wood oil is due the great durability and water-resisting qualities of some of the best varnishes manufactured in the world; in fact, it has been said that the advantage which the Chinese and Japanese enjoyed in producing paints which would dry in damp climates was wholly due to their knowledge of the proper manipulation of china wood oil.

The successful preservation of iron and steel against corrosion by means of a paint film, is not dependent upon any one pigment or upon any one oil; it is rather the successful combination of a number of pigments, and the perfect fusing of the proper oils.

Although suitable inhibitive pigments are limited there are enough available to enable the honest paint manufacturer to utilize them to the fullest extent, and a high-grade anti-rust paint can be made by those who understand the relative value of the right pigments.

It is not so long ago that graphite and carbon paints were considered good protective coatings, but thorough investigation led to the conclusion that they are stimulative on account of the ease with which they conduct electric current. For that reason, they should not be permitted to come in contact with the steel, and should never be used as a priming coat, although, as a second coat, over an inhibitive paint, they are of considerable value.

Red lead, when pure, possesses excellent preservative qualities, but if the red lead is manufactured by what is known as the nitrite of soda process, there will, unless extreme care is used, remain in the red lead a varying percentage of caustic soda. Red lead containing caustic soda makes a very poor paint, since the caustic soda will saponify the

linseed oil, and a short exposure will turn the paint into a pinkish white.

Iron painted with such red lead will corrode rapidly, and it is suggested that the engineer who pins his faith to red lead, specify a red lead containing a minimum percentage of litharge, and absolutely free from caustic soda and nitrite of soda.

Red lead, if free of caustic soda, while theoretically a good pigment, is liable to fail in practice, because of the difficulty connected with its use. The chief objection is that it combines readily with linseed oil, for which reason it must be used "freshly mixed"; otherwise it becomes hard and cakey and unfit for painting purposes. Furthermore, it should be mixed in the proportion of not less than 28 lbs. (33 lbs. gives the best results) to the gallon of oil. The resultant mixture makes a very heavy paint, which is difficult to handle, because of its excessive weight, and the temptation of the painter to add additional thinners is very great, and is generally resorted to.

The fact that in many instances red lead fails to give protection is not due to the red lead itself, but

more often to faulty application and the absence of sufficient red lead in the mixture.

The writer often has observed steel being painted with red lead paint containing about 16 lbs. or less of red lead to the gallon of oil. Such a mixture makes a very poor paint indeed, there not being sufficient red lead present to absorb the oil, and the resulting film of such a paint is bound to have maximum voids, which any engineer knows means minimum strength.

It is refreshing to know that the old-fashioned method of mixing by hand so many pounds of dry red lead and so many gallons of Linseed Oil is rapidly disappearing.

Anyone at all familiar with the painting of steel or iron knows that no hand paddle can thoroughly incorporate the pigments into the oil, and even those who have no knowledge of painting will admit that no hand method can hope to compete in efficiency with modern machinery.

Red Lead is a good pigment, but the amount used in structural iron paints should be subject to

the knowledge and experience of an honest paint manufacturer, and when mixed in proper proportion with some inert pigment such as magnesium silicate or willow charcoal and ground into the oil by means of a modern grinding mill, a more superior paint will be produced than if only Red Lead were used.

Red Oxide is a pigment which is little understood, and to specify "Red Oxide" for the shop coat means little. We might say that the word "Red Oxide" covers a multitude of sins; but while all Red Oxides cover the iron very well, not many cover it for any length of time.

The writer has analyzed many so-called Red Oxide Paints, and in many cases the ferric Oxide (Fe_2O_3) did not exceed ten percent (10%) of the total pigment, the balance being calcium carbonate, calcium sulphate, silica, or magnesium silicate.

The market is crowded with Red Oxides. We have many varieties of Domestic Red Oxides, and since the European War was so successfully terminated, we again have available Spanish and Persian Gulf Oxides.

The value of Red Oxide as a pigment for steel or iron depends upon the percentage of iron (Fe_2O_3) it contains. Natural high-grade Oxides usually contain from 75% to 85% Fe_2O_3 , and such Oxides are valuable pigments in a structural iron paint, but they must be used with discretion, and should be well ground into the proper vehicle.

There are obtainable Artificial Oxides of 99% purity, but such Oxides are generally made by the burning of copperas, and very often contain traces of sulphuric acid which have not been eliminated during the burning process. It will be obvious that Oxides containing sulphuric acid should not be used as a pigment for structural iron paints.

Venetian Reds are often sold under the name of Red Oxide. Most Venetian Reds are made by calcination of copperas and lime, the reaction forming ferric oxide and calcium sulphate. The percentage of (Fe_2O_3) in such reds vary from 15% to 40%, the balance being calcium sulphate. Since calcium sulphate is of a very soluble nature and is readily ionized in the presence of water, the writer considers it a dangerous pigment for steel or iron.

Graphite paints are no longer a factor in connection with priming coats for iron and steel, for it is well understood that they are stimulative rather than preventative. Graphite conducts electricity quite readily, and for that reason alone should not be brought in contact with steel or iron, although there are other objections well worth mentioning.

Graphite is a very slow drier and requires excessive amounts of driers to be added. It is a greasy, slippery pigment, for which reason it has rather large covering capacity, but the resulting film is too thin and too porous to afford protection for any length of time. Its smooth finish is a serious defect, because it makes it poorly adapted for repainting, since other paints when applied over graphite do not seem to adhere properly.

Carbon paints are like graphite paints—dangerous when used as a priming coat for steel or iron, principally because, like graphite, carbon is a good conductor of electricity, but in the writer's opinion it has an advantage over graphite when used over an inhibitive paint, as it lends itself better to repainting.

Lamp Black, which is made from the combustion of oil, is a very pure carbon, often being over 99% pure, and while as a second coat over an inhibitive paint it has considerable merit, it should not be used as a priming coat on iron or steel, since it has a high conductivity.

Bone Black is["] manufactured by grinding animal bones and then burning same in highly heated iron retorts. It is considered by the writer an excellent inhibitive and is used by him in place of carbon or lamp black in the well-known anti-rust paint manufactured by his Company.

Willow Charcoal is a pigment made from the charring of willow wood, and besides making a very good inhibitive pigment, it is also recommended for those who occasionally suffer from indigestion. It usually contains traces of alkali, which no doubt accounts for the splendid inhibitive qualities it possesses.

Practically all chromate pigments are valuable as inhibitors, although care must be taken that they are free from acids, and those manufacturers

who have learned the value of chromate pigments must be prepared to carefully test them before using them.

There are other pigments which might deserve to be specifically mentioned, but since the writer is engaged in the manufacture of a high-grade, well-known anti-rust paint, he cannot be expected to lay bare all the facts which years of study and practical experience have brought forth.

The object of this booklet is not to recommend a specific paint, but rather to present to those who are interested in the subject a brief outline of the facts in connection with the problem civilization must solve.

CHAPTER IV

Stimulative and Inhibitive Pigments

When the writer had become once convinced that the electro-chemical explanation of corrosion was the correct one, a number of experiments were immediately undertaken.

The first important problem was to determine the chemical relation of various pigments heretofore used in structural iron paints.

During the research work, it was found that certain pigments when brought in contact with iron had a tendency to excite electrical action and stimulate corrosion, while other pigments possessed ability to inhibit or retard corrosion.

That certain pigments would inhibit corrosion was made clear by Wood (I) as early as 1895, at which time he commented on the power of paints and pigments containing certain oxidizing agents, notably potassium bichromate and lead chromate, to form on iron and steel surfaces a thin coating of

(I) Am. Soc. Mech. Eng. Trans., 1895, 16,671.

oxide which so effectually protects the metallic surfaces from corrosion that after the removal of the paint the metal still resists atmospheric effects for a long time, as well as the stronger effect of immersion in sea-water or acidulated waters and sulphurous and other vapors.

It seemed desirable to demonstrate by a careful test whether certain pigments in the presence of water would actually stimulate corrosion, and the following experiment was undertaken:

Three sets of fifteen 10-oz. wide neck bottles were carefully cleaned and grouped in four sections,—two sections of 20 bottles each, one section of three bottles and one section of two bottles.

It was thought advisable to determine whether distilled water had any advantage or disadvantage over natural water, so in the first and third sections distilled water was used, and in the second and fourth section water taken from the Allegheny River.

The bottles were numbered as follows:—first section 1 to 20; second section 21 to 40; third section 41 to 43, and fourth section 44 to 45.

Into each bottle numbered from 1 to 20 was placed a measured amount of one of the 20 pigments selected, after which 5 oz. of clear distilled water was added.

Into each bottle numbered from 21 to 40 was placed the same amount and kind of pigments as in Bottles 1 to 20, after which 5 oz. of water taken from the Allegheny River was added.

Into each bottle numbered 41 to 43 was placed 5 oz. of clear distilled water, and into each bottle numbered 44 to 45 was placed 5 oz. of water taken from the Allegheny River.

Bottles numbered 41, 42, 43, 44 and 45 contained no pigment.

Into each bottle then was placed a piece of steel of the same size and cut from one sheet; each piece was carefully weighed and numbered from 1 to 45.

The bottles were then closed with tight-fitting corks and sealing wax applied to prevent any oxygen from reaching the inside of the bottles, and a period of ten weeks was allowed to elapse, during which time the bottles were not disturbed, though observation was made from time to time.

It was peculiarly instructive to note that in some bottles containing pigments, corrosion of the piece of steel was quite apparent in less than five days, while in other bottles containing pigment, corrosion was not visible through the glass.

Such observations as were possible through the glass did not disclose any material difference in the corrosion of the piece of steel in the bottles containing only either distilled or Allegheny River water.

The most convincing evidence, however, was supplied when the bottles were opened for final examination.

Three hours after the bottles were opened, the pieces of steel were withdrawn, carefully cleaned, dried and weighed, the difference in weight of each piece of steel from the time they were placed in the bottles to the time they were taken out accounting for the quantity of steel which was lost through corrosion.

The pieces of steel which were in bottles 11 and 13 showed almost no loss; those in bottles 31, 32

and 33 were practically free from corrosion. The piece of steel in bottle 12 had corroded quite appreciably, and since bottles 11, 12, 13, 31, 32 and 33 contained chromate pigments, the impression that chromate pigments would actually inhibit corrosion was well confirmed, with the exception of the chromate pigment present in bottle 12.

A further investigation was conducted, and it was found that the cause of the chromate pigment in bottle 12 seeming to stimulate rather than prevent corrosion was due to the fact that the process of manufacturing chromate pigments determines to a large degree whether they are inhibitive or stimulative. The impurities present in the chromate pigment in bottle 12 made it stimulative, and proved conclusively that great care must be used in the selection of chromate pigments when used as a pigment in an anti-rust paint. Careful analysis should be made before the pigment is adopted.

The steel in bottles 1, 2, 6, 7, 8, 21, 22, 26, 27 and 28 showed considerable corrosion. These bottles

contained Lamp Black, Carbon Black, Venetian Red, Graphite, Ochre and similar pigments. The writer does not hesitate to say that the excessive corrosion of the steel in these bottles was directly due to the pigments.

The appearance of the steel in bottles 3, 4, 23 and 24 proved that the pigments in these bottles (Willow Charcoal and Bone Black respectively) were inhibitive in character.

The steel in bottles 5, 9, 10, 14, 15, 16, 17, 18, 19, 20, 25, 29, 30, 34, 35, 36, 37, 38, 39 and 40 had corroded to some extent, but in comparison with the steel taken out of bottles 41, 42, 43, 44 and 45, which, as will be remembered, contained no pigments, it was observed that the corrosion was no more severe, so that the conclusion that these pigments neither stimulated nor retarded corrosion seemed to be justified.

It would be difficult to state positively the difference in action upon the steel of the distilled water or the water taken from the Allegheny River. The writer believes that corrosion was more severe

in the bottles containing distilled water, but no thorough record was possible.

It was a singular fact that almost immediately after the bottles were opened, the water in the bottles without pigments and the water in the bottles containing stimulative pigments assumed a reddish, yellowish color, from which it was deduced that the steel in these bottles had passed into solution prior to additional oxygen reaching the steel in the bottles. This, in the writer's opinion, proves the contention that certain pigments are stimulative because of their activity in decomposing the water, absorbing its oxygen and hydrogen, and conveying same to the steel or iron to cause rust.

It is worthy of note to mention that proportionately the steel in the bottles containing only water and in those bottles containing stimulative pigments corroded more in the three hours the bottles were left open than in the entire period they were sealed. It is thus fair to assume that if a supply of free oxygen had been available continuously, corrosion would have been more severe.

There was absolutely no change in the steel placed in bottles containing chromate pigments, with the exception of bottle No. 12, and an explanation for this particular case has been given above.

The test just described was duplicated a few months later, but before the pigments were added to the water, all oxygen was removed from the inside of the bottles. The general results of corrosion, when later on oxygen was introduced, were so similar that no material change in deductions could be recorded.

A very unique test was recently completed by the writer. A wooden tank, 12 x 4 x 4, was filled with a salt water solution. Seven (7) strips of sheet steel, each painted with a different paint made from inhibitive and stimulative pigments, were immersed in the solution, connected to each other by means of wire, and suspended into the solution from wire hooks, which in turn were placed on ordinary gas pipe resting on each end of the tank.

The wires connecting the strips were not painted, although care was taken to properly paint the edges

of the holes in the strips of steel. The same procedure was followed in regard to the wire hooks resting on the gas pipe, so that no single spot on the strips of steel was unprotected.

Strips 1, 2 and 3 were painted with a paint containing chromate pigments ground into a "special" vehicle consisting of linseed oil, china wood oil and varnish gums.

Strip No. 4 was painted with a chromate pigment paint, the vehicle of which was pure linseed oil with the necessary amount of drier.

Strips 5 and 6 were painted with such pigments as former test had shown to be stimulative, ground into a vehicle consisting of pure linseed oil and drier.

Strip No. 7 was painted with a combination of pigments used on Strips 5 and 6, ground into a vehicle consisting of linseed oil, china wood oil, and varnish gums.

The strips were left in the solution for fifteen days, after which careful observation was made.

Strips 1, 2 and 3 were still perfect.

Strip No. 4 showed a slight decomposition of the paint film.

Strip No. 5 also showed a slight decomposition of the paint film.

The paint on Strip No. 6 had suffered more than that on Strip No. 5; and the paint on Strip No. 7 was still in excellent condition.

The strips were again placed into the solution, and results recorded each day.

After twenty days, the paint film on Strips 4, 5 and 6 began to fail rapidly, and on the twenty-fifth day rust became noticeable on Strips 5 and 6. Strip No. 4 did not show any rust. Strips 1, 2 and 3 were at that time still perfect.

After forty-eight days the film on Strip No. 7 showed evidence of breaking, and three days later rust was observed.

This test was extended over a period of seventy-five days, and the final results as shown on the

STIMULATIVE AND INHIBITIVE PIGMENTS

table below are of considerable interest:

<i>Strip</i>	<i>Condition</i>			
1	Excellent	Excellent	Excellent	Excellent
2	Excellent	Excellent	Excellent	Excellent
3	Excellent	Excellent	Very Good	Very Good
4	Very Good	Very Good	Good	Fair
5	Good	Fair	Bad	Very Bad
6	Good	Fair	Bad	Very Bad
7	Excellent	Very Good	Good	Good
	15 Days	25 Days	50 Days	75 Days

This test proved:

1. That the proper chromates ground into the right kind of vehicle will retard corrosion.
2. That the proper chromates ground in linseed oil will to a certain extent protect the steel against corrosion even after the oil film has ceased to give protection.
3. That certain pigments will stimulate corrosion, and that a pure linseed oil film is not entirely free from pores.
4. That stimulative pigments cannot set their hostile forces to work until the vehicle permits moisture to come in contact with the pigments.

Anyone will appreciate that a seventy-five day submersion in a salt-water solution is a very severe test for any paint, and the resistance to salt water developed by the "Special" vehicle used in this test was particularly gratifying to the writer. It

is only fair to add that this "Special" Vehicle is the vehicle used in the well-known anti-rust paint manufactured by the writer's company.

To those who desire to make a rather simple test of the inhibitive character of some and the stimulative tendency of other pigments, the following experiment is suggested:

Place a teaspoonful of some of the better known pigments, such as graphite, lamp black, yellow ochre, red lead, zinc oxide, zinc chromate, lead chromate, willow charcoal, bone black, and iron oxide in a 4-oz. wide neck bottle, and add from 2 to 3 ounces of water. Place in the bottles a piece of steel or iron (an ordinary nail will do), using care that the piece of steel or nail is free from corrosion. It is advisable to place the nail or the piece of steel in the bottles with the aid of a pair of pliers or string, so that the acid of the fingers might not cause corrosion.

Put a tight-fitting cork in the bottle, and allow the bottle to remain undisturbed.

In time you will observe that the steel or nail in some bottles will corrode more rapidly than in

others, and you will find that the steel or nail in some bottles will not corrode at all.

This simple test will enable anyone to distinguish inhibitive from stimulative pigments.

This test can also be made by eliminating the pigments, and by inserting in the bottles pieces of steel painted with the different kinds of paint recommended for steel and iron. The latter test may be advisable, as it will give a comparative test of the relative merit of a number of paints on the market.

Recently there has been introduced a test which anyone can make, and which, if carefully conducted, will show remarkable results. The purpose of this test is to determine the properties of the pigments tested in their relation to the formation of rust when applied to steel and iron as part of a protective coating. The test is carried out as follows:

Each pigment selected is mixed to a soft paste with water. A sufficient number of Gillette Razor Blades (one for each pigment to be tested) are

carefully rubbed with fine emery and weighed. One blade is then embedded in each paste and wrapped with an absorbent paper which will provide perfect contact between the paste and the metal.

This package is now placed in a box lined with blotting paper and wetted daily. The package should remain in the box for about fifteen to twenty days, after which the blade is unwrapped, carefully washed free of pigments, and re-weighed.

The condition of the blade is then noted and the loss of weight calculated. Whatever loss of weight has taken place has resulted from the formation of rust, and of course the greater the loss the greater the amount of rust which was formed.

This test will conclusively show that some pigments cause a greater loss than others, and fairly correct data concerning the stimulative and inhibitive qualities of pigments can thus be obtained.

CHAPTER V

The Law of Maximum and Minimum Voids

A paint designed to protect wood will stand guard against decay just so long as it prevents moisture from reaching the surface over which the paint is applied.

In recent years, much attention has been given to the so-called reinforcing of linseed oil when used as a vehicle for house paint, and splendid results have been obtained.

The modern paint manufacturer has in view only one object, and that is to increase the life of his product; and since the veil of secrecy (which for many years was in vogue in the paint and varnish industry) has been allowed to be lifted, much research work has been conducted on what might be termed a co-operative scale.

Co-operation is conducive of progress, and so we have today a pretty thorough understanding of the underlying principles of modern paint-making.

Like any industry, the paint and varnish industry has its pioneers, and due to their efforts,

greater progress will undoubtedly be made, but it will be admitted that enough information is available to enable the reputable manufacturer of house paints to furnish a product of real merit.

It is unfortunate that the manufacture of structural iron paints is not so generally understood. At least, one is compelled to reach that conclusion when the different kinds of structural iron paints offered for sale are subjected to a close examination. While individual efforts have been directed to the perfection of a real anti-rust paint, no general revival has taken place, and today graphite paints are recommended pretty much like they were before it was discovered that they are stimulative. The same holds true insofar as carbon and similar paints are concerned.

Since moisture is always the deciding factor in either the decay of wood or the corrosion of iron and steel, it must be obvious that all care must be directed to prevent moisture from reaching the surface.

A linseed oil vehicle can be made more waterproof by the addition of certain varnish gums,

which however must be added under conditions which should be thoroughly understood and with extreme care and discretion. The oil must be heated to the proper degree and the gums incorporated at the right time, and the degree of heat necessary can only be determined through careful and tedious experimenting. Those of us who have given this subject attention know the efforts required and are not unmindful of the caution which must be exercised.

It is not fair to expect a certain part of a combination to stand all the strain or to bear the entire burden; consequently, no one should expect the vehicle in a structural iron paint to shoulder all the responsibility. A man should not, in fact, does not expect his wife to be the housekeeper and the breadwinner (although some of us have tried to get away with it), because, if the wife was willing or able to assume both jobs (and housekeeping really is a job) she would not need, or desire, to have one of us poor men as a partner; and for the same reason, if the vehicle in a paint is to do the entire

job, the rest of the combination (pigments) are not required.

Pigments, however, are needed, and their proper selection for different paints constitutes an important part of modern paint-making.

That certain pigments, by virtue of their catalytic action upon the oil, shorten the life of the oil, is now well recognized; hence, such a pigment must either be eliminated altogether, or its harmful effect should be counteracted with some other pigment. The presence thus of more than one pigment is often desirable from a chemical point of view, but from a physical point of view, it is absolutely essential.

Anyone with but a superficial knowledge of physics, will understand that the mixing with a liquid of one pigment (the particles of which are all of the same size) will produce a mass or film having maximum voids, and maximum voids means minimum strength.

In a paint film, the law of maximum and minimum voids is very important, because the more

voids in the film, the more weak spots will be open to the attack of moisture and other injurious elements.

Furthermore, the combination of several correct pigments assist materially in making the paint film resistant to moisture, and by so doing, these pigments are instrumental in increasing the life of the paint.

Cement is a very necessary ingredient in concrete up to a certain quantity, but the more we exceed the necessary quantity, the more will we weaken the tensile strength of the concrete. So it is with a paint film—a combination of pigments will outlast a single pigment, no matter how excellent this one pigment may be.

No one will deny that white lead is a splendid pigment, but anyone interested can easily satisfy himself that pure white lead and linseed oil cannot successfully compete in lasting qualities against a mixture of white lead, zinc oxide and a small percentage of either barium sulphate, silica, or magnesium silicate and linseed oil.

Paint, as well as cement, requires reinforcing. In concrete we use sand and gravel; in paints, besides zinc oxides, there are many so-called inert pigments which are indispensable, and expert knowledge of these pigments on the part of the paint manufacturer will enable him to deliver an article of superior merit.

Structural iron paints should never consist of one pigment, mainly because such a paint film would have maximum voids, and moisture would soon destroy its usefulness.

An extensive test conducted by the writer, which covered a period of years, demonstrated conclusively that no single pigment paint can compare in efficiency with a properly balanced paint containing from three to five pigments, and those paints containing varying percentage of chromate pigments proved most effective in the prevention of corrosion.

CHAPTER VI

Protection Against the Action of Sea Water

The problem of protecting against corrosion steel work exposed to sea water is of such great importance that the writer feels it necessary to include a special chapter.

The soluble salts present in sea water will penetrate through ordinary paint films in a very short time, and if such paints contain pigments which are stimulative in nature, galvanic action will proceed at an alarming rate. It is not difficult to account for this, since these soluble salts will not only dissolve the paint film but will readily ionize, thereby causing, with the aid of such pigments, electrical charges to flow from the point of maximum to the point of minimum solution pressure. A solution of salt will readily conduct a current of electricity, which is accounted for by the fact that the salt is dissociated into ions.

Inhibitive pigments therefore should always be present in a paint designed to withstand the action of sea water.

While obviously the pigments constitute a very important factor, the selection of the vehicle is of even greater consequence. Straight pure Linseed Oil will not fill the bill,—first, because such a film would not be free from pores, and, second, because its resistance to sea water is not very great. This statement should not be interpreted as a reflection upon Linseed Oil, because sea water has been known to penetrate the hardest paint film. It is the writer's opinion that for many purposes, Linseed Oil stands in a class by itself and cannot be replaced. It is only fair, however, to recognize its few weaknesses while crediting it with many excellent qualities.

The action of sea water is extraordinary and the protective coating should therefore be no less extraordinary.

All possible research should, and in individual cases, has been directed to the perfection of a vehicle resistant to the action of the soluble salts which constitute a part of sea water. Water-excluding properties should be its predominating virtue, and

special attention should be directed to making the vehicle impervious to the soluble salts.

Expert manipulation of linseed oil, china wood oil and certain varnish gums will make the production of such a vehicle possible, and it is a matter of record that a vehicle perfected by the writer showed remarkable resistance to sea water.

One thing is certain—the electrolytic theory is applicable in no case so convincingly as it is in the corrosion of iron and steel subject to the attack of sea water.

CHAPTER VII

Concrete as a Protector Against Corrosion

The question whether structural steel ultimately to be imbedded in concrete should be protected against corrosion by means of a paint film is a much debated one.

Many engineers, basing their opinion upon past experience, claim that concrete is a perfect insulator against corrosion, and under many circumstances, the writer agrees with that view.

It is a well known fact that iron does not rust in a highly alkaline solution, although rusting proceeds dangerously when the alkalinity is not high enough. Before corrosion can proceed, however, it is necessary that oxygen comes in contact with the steel, and it seems reasonable to assume therefore that steel imbedded in concrete, provided oxygen cannot reach the surface, is effectively protected against corrosion by the concrete or cement.

There, most generally, is sufficient alkali in the concrete to afford protection, and the writer has

seen many examples of steel imbedded in concrete for many years, which upon removal of the concrete was in perfect condition.

There usually are spots where corrosion is very severe, but these spots are localized and generally occur only where the steel rises above the grade line, at a joint, or where crevices in the concrete allowed oxygen and moisture to reach the steel.

Such experiments as the writer has made, and such observation as has come to his attention would seem to justify him in stating that where the structural steel is comparatively free from corrosion at the time the concrete is poured, and where the concrete is of sufficient density to prevent oxygen from reaching the steel, and provided that a perfect bond between the steel and the concrete is assured no fear for corrosion need to be entertained.

It must be obvious to anyone that a bond between the steel and the concrete is essential. Concrete will adhere perfectly to steel when comparatively free from corrosion, but if corrosion is appreciable at the time the concrete is applied, a

perfect bond will not be obtained, and corrosion might proceed, with the added danger that it is likely to cause the concrete to crack, which, if so, would increase the corrosion because the porous or cracked concrete would permit water to find its way to the steel.

Delays not anticipated at the time the work was undertaken might necessitate lengthy postponements, during which time the unprotected steel might be exposed for a long time, and of course corrosion would be very severe, and such steel would really be unfit to receive concrete.

The writer knows of one case where approximately 3000 tons of steel were allowed to remain at the building site for more than two years before erection could proceed. At the time the steel was ordered everything pointed to immediate erection and subsequent application of concrete, consequently the steel was ordered unpainted. When it was possible to resume work, the steel was in such terrible condition due to corrosion that it was considered hopelessly deficient for the purpose originally intended. The only way which remained open

was to thoroughly clean and paint the steel, which was subsequently done, but at a cost which exceeded by many thousand dollars the nominal charge for which that same steel could have been painted in the shop prior to shipment.

Such an occurrence is by no means uncommon, and it would therefore seem that the Engineer in charge of the work is best qualified to determine whether steel to be embedded in concrete should or should not be painted in the shop prior to shipment.

If the steel can be imbedded in concrete before excessive corrosion takes place, painting is not essential, but since the application of a shop coat can be secured at a cost insignificant compared to the benefits derived, it seems that prudence would suggest a course of certainty rather than that of uncertainty.

Careful consideration, however, should be given to the character of the paint best suited for the purpose.

Linseed oil paints are of no use; in fact, their use would be detrimental, since linseed oil is a saponifiable oil. The writer has on many occasions

demonstrated that the alkali in the cement will saponify and destroy the linseed oil, by virtue of which a bond between the concrete and the steel is prevented.

A very interesting experience of a well-known Construction Engineer related by him to the writer conclusively proves the accuracy of the above statement, and while the case in question may be an unusual one, the evidence secured was so convincing that the writer cannot forego the pleasure of imparting it to his readers.

Some years ago this Engineer was in charge of the erection of a large warehouse. This warehouse was designed for the storing of heavy materials, which necessitated the use of very heavy beams for the floors, on which the shop paint was Red Lead in Oil. The building had concrete floors, and the floor beams were encased in concrete.

Some weeks after the concreting had been done it was discovered that a mistake had been made in the spacing of the floor beams, and they had to be taken out in order to correct the error. The job

of getting the floor beams out of the mass of concrete was anticipated with a great deal of anxiety, because it was thought that the floor consisted of a solid mass of concrete and steel. Imagine, therefore, the surprise of everybody when it was found that the beams could be taken out of the concrete in the same manner that one could withdraw a warm knife out of a mass of butter. The beams were literally pulled out of the concrete, since there wasn't the slightest resemblance of a bond between the floor beams and the concrete.

This incident certainly substantiated in unmistakable terms the writer's claim that a linseed oil paint is totally unfit for steel which is to be imbedded in concrete.

Paint designated for this purpose should contain only non-saponifiable oils, so that no chemical reaction takes place when it comes in contact with the concrete; it must also provide a bond between the steel and the concrete, and dry with a waterproof film. China wood oil can be successfully employed and the selection of proper pigments can make such a paint highly rust resisting.

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